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(54) Title: PIGMENT COMPOSITIONS FOR OIL-BASED LITHOGRAPHIC PRINTING INK SYSTEMS

(57) Abstract: Pigment compositions for oil-based lithographic printing ink systems are provided which comprise as colourant a mixture of an organic pigment and an organic dyestuff soluble in an organic solvent (solvent dye). The printing inks prepared from these pigment compositions show outstanding improvements in colour strength combined with improvements in both gloss and transparency of the prints obtained.



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## Pigment Compositions for oil-based Lithographic Printing Ink Systems

The present invention relates to pigment compositions suitable for use in oil-based lithographic printing inks. More particularly, the invention relates to pigment compositions containing a combination of an organic pigment and an organic dyestuff soluble in an organic solvent (solvent dye).

Lithographic printing is a process which utilizes a coated metal or polymeric plate containing a hydrophobic image area which accepts hydrophobic based ink and a non-image hydrophilic area which accepts water, i.e. the fountain solution.

Traditional pigment-based inks for off-set lithographic printing require as a rule an increased level of pigmentation in order to achieve higher colour strength. Increases in pigment loading result, however, in both manufacturing and performance problems.

A high pigment loading may cause various difficulties, such as a reduced dispersibility of the pigment resulting in oversize pigment particles and grit, or a small wetting performance of the pigment. Poor wetting and dispersion lead, on the other hand, to poor colour strength, and further, increased shear rate is required during the manufacture of the inks to achieve the desired dispersion and to overcome the viscosity.

Other problems that derive from high pigment loadings and/or high viscosity of the inks may be poor transfer and distribution on the printing press rollers, and a considerable reduction of the film-forming properties of the printing inks. And finally, high pigment loaded inks may lead to prints of poor transparency and gloss.

An alternative approach to increased colour strength would be to increase the thickness of the ink film though this results in further problems.

Increased film thickness can result in prints that are more difficult to dry or cure, further a lower transparency and a reduced printed image definition can be observed. Another problem that can be caused by an increased ink film thickness relates to the achievement of a correct ink/water balance on lithographic presses thus leading to printability problems.

And also, increased ink film thickness results in greater expense in that shorter press runs are possible only and more frequent ink supply changes are needed.

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It has now been found that these problems can be overcome and outstanding effects with regard to e.g. increased colour strength, but also improved gloss and transparency of the prints obtained, and improved printing performance, can be achieved when using the new organic pigment/solvent dye compositions, hereinafter described, in lithographic printing ink systems.

Lithographic printing ink based purely on solvent dyes can be prepared but these do not show any strength advantage over pigment based inks.

Accordingly it is the main object of the present invention to provide said new lithographic printing ink compositions comprising organic pigment/solvent dye mixtures. Other objects of the present invention relate to processes to prepare said compositions, to prepare printing inks from said compositions, the thus obtained printing inks, and the use of said inks in lithographic printing processes. These and other objects of the present invention will be described in the following.

Therefore, in a first aspect of the present invention, there is provided a lithographic printing ink composition, which comprises a mixture of an organic pigment and an organic dyestuff soluble in organic solvents (solvent dye) and printing ink varnishes (ink vehicles), solvents and other customary additives, the printing ink varnishes or additives being mixed or coloured with the solvent dye either prior to or during pigment dispersion.

This particular combination of an organic pigment and a solvent dye (normally being of the same shade) - when incorporated in a printing ink for lithographic printing systems - results in an ink which displays synergistic effects, e.g. with regard to higher colour strength and printing performance.

Pigment dispersion should be considered as the process of deaggregation, wetting and incorporation of pigment particles into a varnish medium such that the medium appears to be coloured throughout.

The pigments are those producing the four colours commonly used in the printing industry: namely black, cyan (blue), magenta (red) and yellow. As a rule, they are compatible with the other components of the inventive ink compositions and constitute the basis (colourant) for forming the oil-based printing inks for lithographic printing processes, which are another object of the present invention.

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Organic pigments comprise such as, but not exclusively, monoazo, disazo, azomethine, azocondensation, metal-complex azo, naphthol, metal complexes, such as phthalocyanines, dioxazone, nitro, perinone, quinoline, anthraquinone, hydroxyanthraquinone, aminoanthraquinone, benzimidazolone, isoindoline, isoindolinone, quinacridone, anthrapyrimidine, indanthrone, flavanthrone, pyranthrone, anthanthrone, isoviolanthrone, diketopyrrolopyrrole, carbazole, perylene, indigo or thioindigo pigments. Mixtures of the pigments may also be used.

The disazo pigments represent an important class of colouring materials commonly used for the manufacture of lithographic printing inks. Preferably they are yellow and orange diarylide pigments and orange disazopyrazolone pigments, including e.g. the C.I. (Colour Index) Pigment Yellows 12, 13, 14, 17, 83, 174, and 188, as well as the C.I. Pigment Oranges 13 and 34 which are often used as shading agents.

Preferred blue pigments are e.g. metal complexes, such as copper phthalocyanine pigments (e.g. C.I. Pigment Blue 15:3), while the red pigments are e.g. the naphthol pigments, preferably  $\beta$ -naphthol or  $\beta$ -oxynaphthoic acid (BONA) pigments (e.g. C.I. Pigment Red 57:1).

For further details as to all these organic pigments reference is made to *Industrial Organic Pigments*, W. Herbst, K. Hunger, 2<sup>nd</sup> edition, VCH Verlagsgesellschaft, Weinheim, 1997.

The pigments can carry surface treatments in order to improve their performance within the chosen ink system. Typical additives for surface treatment are, for example but not exclusively, the rosin acids, ionic or nonionic surfactants and ionic dyestuffs. The appropriate selection of pigment additives and those for surface treatments suitable for the chosen ink system can be carried out by one skilled in the art.

"Solvent Dye" is a term well known in the art and defined in the Colour Index (C.I.), published by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists.

As to the chemical constitution of the solvent dyes the monoazo and disazo, and also some polyazo dyes predominate. Other important dyes are xanthene, triarylmethane, anthraquinone, azine, thiazine and phthalocyanine dyes.

Representative red dyes include the C.I. Solvent Reds 19, 23, 24, 25, 26, 27 and 29 (which all are disazo dyes), further the C.I. Solvent Reds 1, 49, 52 and 111.

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Representative blue dyes include the C.I. Solvent Blues 14, 35, 36, 59 and 78.

Representative yellow dyes include the C.I. Solvent Yellows 7, 14, 33, 72, 94 and 114.

Representative orange dyes include the C.I. Solvent Oranges 1, 2 and 7.

- 5 Mixtures of said Solvent dyes can also be used. Examples are 1:1 mixtures (by weight) of C.I. Solvent Reds 26 and 27, or 1:1:1:1 mixtures of C.I. Solvent Reds 23, 24, 26 and 27.

10 The pigment/solvent dye ratios comprise as a rule (99-1) : (1-99), preferably (98-10) : (2-90) and most preferred (95-30) : (5-70). Within this last range, the ratio of (95-65) : (5-35) is of special interest.

15 The inventive pigment-based lithographic printing inks may contain 0.1 to 70% by weight (all percentages mentioned below are by weight) of the inventive pigment/solvent dye composition, the remainder being customary printing ink-varnishes (ink-vehicles), solvents and other suitable and well known additives. The 0.1 to 70% range covers concentrated and ready-to-use printing inks. For actual use, the concentrated printing inks are diluted with suitable solvents, resins, varnishes (ink vehicles) or varnish/ink vehicle components.

20 Preferred are percentages of 2 to 55%, mostly preferred of 2 to 20%; for normal preparation methods (printing inks ready for use) the range of 12 to 18% is of special interest, while the 20 to 70%, preferably 20 to 55%, range is for concentrate production.

Within this preference range of 20 to 55%, concentrate production by bead-mill is preferably carried out with said compositions of 20 to 35% pigment/solvent dye content; whereas for a production by kneader the corresponding preferred range is 35 to 55%.

25 These concentrates, which can also be prepared at various concentrations by extrusion, can be the basis for preparing the inks, e.g. by dilution, used for the actual printing process.

30 Another inventive embodiment comprises lithographic printing ink colourants, which comprises a mixture of an organic pigment and an organic dyestuff soluble in an organic solvent (solvent dye) wherein the organic pigment is coated with printing ink varnishes (ink vehicles), solvents and other customary additives, the printing ink varnishes or additives being mixed or coloured with the solvent dye either prior to or during pigment processing.

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These lithographic printing ink colourants can be considered as surface treated (coated) pigment compositions which comprise (highly concentrated) organic pigment/solvent dye combinations, for example containing about 60 to 95%, preferably 70 to 90% of said combination, and about 40 to 5%, preferably 30 to 10% of printing ink-varnishes, solvents and other customary additives mentioned hereinbelow.

The pigment/solvent dye ratio is as mentioned hereinbefore.

They may be prepared by surface treating (coating) the organic pigment with a varnish (ink vehicle) or varnish component, solvent and other customary additives, the vehicle(s) (components) or additives being mixed or coloured with the solvent dye either prior or during processing. The solvent dye may be present in dispersed or dissolved form.

More particularly, the process for preparing these (surface treated and concentrated) lithographic printing ink colourants comprises

(a) incorporating the printing ink varnish, which is premixed or coloured with the solvent dye, into an aqueous slurry of the organic pigment, isolating, and optionally drying it, or  
(b) adding the printing ink varnish to an aqueous slurry of the solvent dye and then combining it with an aqueous slurry of the organic pigment, isolating, and optionally drying it, or

(c) adding the printing ink varnish to an aqueous slurry of a solvent dye/organic pigment combination, isolating, and optionally drying it.

Printing inks for the actual printing process can be obtained e.g. by diluting the concentrates. The printing ink-varnishes (ink vehicles) may comprise, among other components, e.g. high boiling distillates and/or vegetable oils, high wetting alkyd resins plus highly structured alkyd resins and vegetable resins, and mixtures thereof; further monomers/oligomers/polymers that can be cured by UV-radiation can also be used.

The high boiling distillates may be so-called mineral oil solvents which comprise aliphatic or aromatic hydrocarbon distillate fractions of boiling points of from 100 to 350°C, preferably of from 180 to 300°C, or vegetable oils.

The vegetable oils for use in the printing ink vehicles of the invention are the commonly available vegetable triglycerides in which the fatty acid moieties have a chain length of about 12 to 24 carbon atoms, preferably of 18 to 22 carbon atoms. Of particular interest are those

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which have a substantial proportion of diunsaturated linoleic fatty acid and triunsaturated linolenic fatty acid moieties, e.g. soybean, coconut, cottonseed, linseed, safflower, sunflower, corn, sesame, rapeseed and peanut oil or mixtures thereof.

Though the aforementioned oils can be employed in the crude state as originally expressed from the seed material, there are advantages to subjecting them to certain preliminary processing steps. For example, alkali refining removes the gums and phospholipids which may interfere with the properties of the vehicles and the ultimate ink formulations. Alkali refining also removes free fatty acids, which tend to reduce hydrophobicity properties in ink formulations.

The hydrocarbon distillate fractions are preferred, but vegetable oils are also important.

Examples of the resins include long-oil alkyd resins, medium-oil alkyd resins, short-oil alkyd resins, phenol-modified alkyd resins, styrenated alkyd resins, aminoalkyl resins, oil-free alkyd resins, thermosetting acrylic resins, UV-curing resins, acryl laquer resins, acrylpolyol resins, polyester resins, epoxy resins, methylated or butylated melamine resins, vinylacetate copolymers, styrene or styrene-acrylic resins, styrene-diene copolymers, polyurethane resins, rosin (abietic acid), rosin (acid) salts, such as alkali metal salts (sodium, potassium), and modified rosins such as rosin (acid) metal resins (copper, zinc, magnesium resins), rosin esters, such as maleinized rosin, pentaerythritol rosin or rosin-modified phenolic resins, and further vegetable oil based rosin esters, such as soybean or tall oil esters (methyl, butyl), and further hydrogenated rosins, disproportionated rosins, dimerised, polymerised and part-polymerised rosins (rosins, cross-linked with e.g. formaldehyde), or mixtures thereof. These compounds and their use in printing compositions are well known in the art. They are not limitative.

Examples for monomers that can be cured by UV-radiation are, but not exclusively, acrylate monomers, such as 1,4-butanediolacrylate, propoxylated glycerol triacrylate and pentaerythritol triacrylate.

UV-curable monomers can be considered as an ink solvent for the solution of the solvent dyes. Following UV-curing, it can then be considered that the solvent dye remains dissolved or dispersed in the cured resin. As the point of discrimination between ink-solvent and ink-resin activity is flowing, for example partially UV-cured oligomers could be classed as both a solvent and a resin.

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Further details for lithographic printing inks (also known as off-set inks, oil-based inks, distillate based inks or vegetable oil based ink) can be found in "The Printing Ink Manual," 5<sup>th</sup> edition, edited by R.H. Leach and R.J. Pierce, Blueprint (Chapman and Hall), chapter 6, p. 342-452 (1993).

5

The pigment/solvent dye mixtures can be prepared by mixing (grinding) the two components in a conventional manner in solid or liquid state. In the latter case, the solvent dye may be predissolved or dispersed in an organic solvent which may be aliphatic, alicyclic, and aromatic hydrocarbons, halogenated hydrocarbons, esters, ketones, and alcohols.

10

The oil based printing inks for lithographic printing systems can be prepared by incorporating the pigment into the printing ink varnish by a variety of shear rate-inducing methods, such as mixing, bead-milling, triple-roll milling, kneading and extrusion; alternatively, heat-inducing methods can also be used.

15

Examples of typical methodology are triple roll mill, horizontal or vertical bead mill, cobra mill, Z-blade mixer or kneader, single, twin or triple screw extruder and also a Müller glass plate dispersion apparatus.

20

The dyestuff can be dissolved into the varnish by any method allowing the application of heat. This heat can be deliberately applied from an external source. For example, laboratory scale incorporation of the dye can be carried out on a hot-plate or water-jacket heated bead-mill. During the incorporation process, agitation is an advantage though high shear is not essential.

25

Alternatively, the heat can originate from the shearing action and motility of a viscous substrate. For example, the industrial scale bead-milling process on a lithographic varnish often produces heat. This heat production is often greater during the attempted dispersion of pigment as the viscosity of the pigment/varnish mixture is higher.

30

If the pigment incorporation method does not produce heat, the solvent dye is best incorporated by pre-dissolving in a sample of the varnish medium, or one or more of the varnish components or solvents, by the addition of heat.

The preferred method of incorporation would be extrusion. In an ink vehicle (or molten ink vehicle resin) passed through such as apparatus, dispersion of the pigment (by high shear)



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and solution of the dye (by heat generation) can be achieved either simultaneously or sequentially.

The pigment may be applied as either a damp press-cake, dry lump, granule or powder. For  
5 extrusion, the use of granules is currently preferred due to the lower dusting of this pigment form. The solvent dye could similarly be applied as a damp cake, dry lump, granule or powder.

Furthermore, the varnish can be premixed or coloured with the solvent dye and then added  
to an aqueous pigment slurry. Alternatively, the varnish can be added to an aqueous slurry of  
10 the solvent dye or a mixed slurry of the pigment and solvent dye. The obtained lithographic printing ink compositions can then be isolated by filtration and optionally drying; they are one basis for the inventive pigment-based lithographic printing inks.

Alternatively, the solvent dye (as solid or solution in an organic solvent as mentioned) may  
15 also be incorporated by late addition to the finished pigment-based printing ink followed by heating, if necessary to complete solution.

As a further alternative, the pigment-based lithographic printing inks may be prepared by a  
process comprising the flushing of presscakes of pigments or pigment/dye mixtures into a  
20 varnish medium or a pre-dyed varnish medium (printing ink varnish).

The inventive pigment-based lithographic printing inks may in addition comprise customary additives known to those skilled in the art.

Typical additives include drying enhancers, drying inhibitors, non-coloured extenders, fillers,  
25 opacifiers, antioxidants, waxes, oils, surfactants, rheology modifiers, wetting agents, dispersion stabilizers, strike-through inhibitors and anti-foaming agents; further adherence promoters, cross-linking agents, plasticisers, photoinitiators, light stabilizers, deodorants, biocides, laking agents and chelating agents.

Such additives are usually used in amounts of from 0 to 10% by weight, particularly from 0 to  
30 5% by weight, and preferably from 0.01 to 2% by weight, based on the total weight of the lithographic printing ink composition.

The inventive pigment-based printing ink can be used in lithographic printing processes on a lithographic printing press whereby it is e.g. passed from a reservoir by means of a roller duct

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system to the flat substrate to be printed (inking plate). This plate is normally pre-treated with aqueous fountain solution often containing alcoholic components to aid the lithographic process. The printing processes are further objects of the present invention.

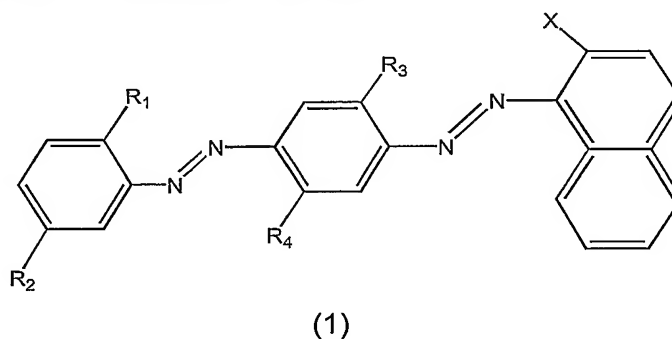
The inventive pigment-based lithographic printing inks lead to an overall good printing performance and produce prints of unexpectedly increased colour strength (compared with an ink based on pigment alone), further improved gloss and transparency in all types of lithographic printing inks known in the art, e.g. heatset, sheetfed, coldset or UV-curing printing inks.

- 10 The present invention is hereinafter further described with reference to particular examples thereof. It will be appreciated that these examples are presented for illustrative purposes and should not be construed as a limitation of the scope of the invention as herein described.

- 15 In the following examples, quantities are expressed as part by weight or percent by weight, if not otherwise indicated. The temperatures are indicated in degrees centigrade.

#### Examples

- 20 The following table shows a selection of red solvent dyes (of the phenylazophenylazo-beta-naphthol class) to be used in the present invention:



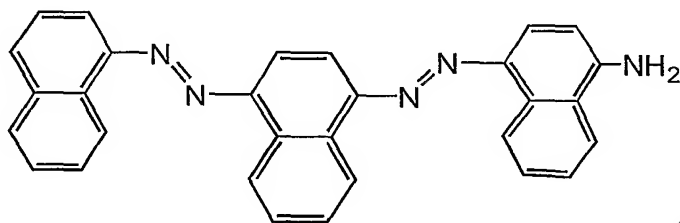
25 Table 1

R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	X	DYE SYNONYMS
H	H	H	H	OH	C.I. Solvent Red 23 Sudan III 1-((4-phenylazo)phenyl)azo-2-naphthol

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CH <sub>3</sub>	H	CH <sub>3</sub>	H	OH	C.I. Solvent Red 24 Sudan IV 1-(4-o-tolylazo-o-tolylazo)-2-naphthol
CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	OH	C.I. Solvent Red 26 Oil Red EGN 1-((2,5-dimethyl-4-((2-methylphenyl)azo)phenyl)azo)-2-naphthol
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	OH	C.I. Solvent Red 27 Oil Red O 1-((4-(dimethylphenyl)azo)dimethylphenyl)azo)-2-naphthol
H	CH <sub>3</sub>	H	CH <sub>3</sub>	OH	C.I. Solvent Red 25 Sudan Red B 1-((3-methyl-4-((3-methylphenyl)azo)phenyl)azo)-2-naphthol
H	H	H	H	NHCH <sub>2</sub> CH <sub>3</sub>	C.I. Solvent Red 19 Sudan Red 7B N-ethyl-((4-(phenylazo)phenyl)azo)-2-naphthylamine

Further dyes can be found in "The Colour Index published by The Society of Dyers and Colourists". C.I. numbers for these red dyes are 26000-26150. The structure of a further applicable red dye (C.I. Solvent Red 29) found within this C.I. number selection is shown below (Formula 2).



(2)

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## EXAMPLE 1

## Ink A

24g of 1-((4-((dimethylphenyl)azo)dimethylphenyl)azo)-2-naphthol is incorporated into 141.75g of a commercial heat-set varnish composition by high shear bead-milling which  
 5 leads to the composition experiencing a temperature of 80°C for a period of 15 minutes.

## Ink B

27g of a C.I. Pigment Red 57:1 composition tailored for heat-set use is incorporated into 141.75g of a commercial heat-set varnish by an identical method to Ink A.

## Ink C

10 23g of 1-((2,5-dimethyl-4-((2-methylphenyl)azo)phenyl)azo)-2-naphthol is incorporated into 141.75g of a commercial heat-set varnish by an identical method to Ink A.

## Ink Blends

Blends of inks A and B plus also blends of inks B and C are prepared by 2 series of 25 revolutions on a Müller glass plate dispersion apparatus. The instrumental strength at 510-  
 15 550nm for each blend is compared against the standard pigment-only ink B (which is given the figure of 100%) by Prufbau printing. Key Prufbau prints are also compared visually and assigned strength figures against standard in 5% increments.

20 Table 2

Ink A	Ink B	Ink C	Instrumental Strength	Visual Strength
-	100	-	100%	100%
10	90	-	114%	110-115%
20	80	-	116%	115%
30	70	-	112%	-
50	50	-	110%	-
70	30	-	105%	-
100	-	-	94%	-
-	90	10	111%	110%
-	80	20	121%	120%

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-	70	30	123%	125%
-	50	50	119%	-
-	30	70	110%	-
-	10	90	104%	-
-	-	100	97%	-

#### Pigment/Solvent Dye Blends – Additional Benefits

As examples of the additional benefits achievable by the incorporation of even relatively small amounts of dyestuff, prints from the 90/10 and 80/20 ink B/ink A blends show slightly improved gloss and transparency over ink B alone.

Furthermore, an 80/20 ink B/ink A blend shows reduced water emulsification and reduced bleed colouration in comparison with pure ink B.

Similar effects are found from the 90/10 and 80/20 ink B/ink C blends. Furthermore, the 70/30 ink B/ink C blend displays a significant improvement in both gloss and transparency over ink B alone.

#### Example 2

A coloured ink vehicle is prepared by combining together 42.0g of a commercial heat-set lithographic varnish with 0.80g of 1-((4-(dimethylphenyl)azo)dimethylphenyl)azo)-2-naphthol and heating to a temperature between 80°C and 105°C for a period of 15 minutes. 0.856g of this ink vehicle is then combined with 0.144g of a C.I. Pigment Red 57:1 composition tailored for heat-set use using 2 series of 75 revolutions on a Müller glass plate dispersion apparatus.

#### Example 3

The procedure of example 2 is repeated with 1-((4-(dimethylphenyl)azo)dimethylphenyl)azo)-2-naphthol being replaced by 1-((2,5-dimethyl-4-((2-methylphenyl)azo)phenyl)azo)-2-naphthol.

#### Example 4

The procedure of example 2 is repeated with 1-((4-(dimethylphenyl)azo)dimethylphenyl)azo)-2-naphthol being replaced by 1-(4-o-tolylazo-o-tolylazo)-2-naphthol.

## Example 5

The procedure of example 2 is repeated with 1-((4-(dimethylphenyl)azo)dimethylphenyl)azo-2-naphthol being replaced by 1-((4-phenylazo)phenyl)azo-2-naphthol.

## 5 Example 6 (Comparative Example)

42.0g of a commercial heat-set lithographic varnish is heated to a temperature between 80°C and 105°C for a period of 15 minutes to mimic the conditions experienced in examples 2-5. 0.840g of this heated material is combined with 0.160g of a C.I. Pigment Red 57:1 composition tailored for heat-set use using 2 series of 75 revolutions on a Müller glass plate dispersion apparatus.

## Results of Examples 2-5:

Examples 2, 3, 4 and 5 are each drawn down and assessed visually against comparative example 6 as a standard. All show superior colour strength to standard.

## 15 Example 7 (Comparative Example, for Examples 8 and 9)

27.00g of a C.I. Pigment Red 57:1 composition tailored for heat-set use is incorporated into 141.92g of a commercial heat-set varnish by a method involving high-shear bead-milling which leads to the composition experiencing a temperature of 60°C or over for 30 minutes.

## 20 Example 8

Comparative Example 6 is repeated where 10% of the pigment is replaced by a 1:1 blend of 1-((3-methyl-4-((3-methylphenyl)azo)phenyl)azo)-2-naphthol and 1-((2,5-dimethyl-4-((2-methylphenyl)azo)phenyl)azo)-2-naphthol. On printing, the ink gives an increase in strength of 15% over Comparative Example 7.

## Example 9

Comparative Example 7 is repeated where 10% of the pigment is replaced by a 1:1:1:1 blend of 1-((4-phenylazo)phenyl)azo-2-naphthol, 1-(4-o-tolylazo-o-tolylazo)-2-naphthol, 1-((3-methyl-4-((3-methylphenyl)azo)phenyl)azo)-2-naphthol and 1-((2,5-dimethyl-4-((2-methylphenyl)azo)phenyl)azo)-2-naphthol. On printing, the ink gives an increase in strength of 20% over Comparative Example 7.

## Claims

1. A lithographic printing ink composition, which comprises a mixture of an organic pigment and an organic dyestuff soluble in organic solvents (solvent dye) and printing ink varnishes (ink vehicles), solvents and other customary additives, the printing ink varnishes or additives being mixed or coloured with the solvent dye either prior to or during pigment dispersion.
2. The composition according to claim 1, wherein the pigment/solvent dye ratio is (99-1) : (1-99), preferably (98-10) : (2-90), and most preferred (95-30) : (5-70).
3. The composition according to claim 1, wherein the pigment/solvent dye ratio is (95-65) : (5-35).
4. The compositions according to any one of claims 1 to 3, which comprises mixtures of solvent dyes and/or mixtures of organic pigments.
5. A pigment-based lithographic printing ink, which comprises the compositions according to any one of claims 1 to 4.
6. The pigment-based lithographic printing ink according to claim 5, which comprises 0.1-70%, preferably 2 to 55%, of an organic pigment/solvent dye mixture, and the remainder being printing ink varnishes, solvents and other customary additives.
7. The ready-to-use pigment-based lithographic printing ink according to claims 5 or 6, which comprises 2 to 20%, preferably 12 to 18%, of the organic pigment/solvent dye mixture.
8. A concentrated pigment-based lithographic printing ink according to any one of claims 5 to 7, which comprises 20 to 70%, preferably 20 to 55%, of the organic pigment/solvent dye mixture.
9. The pigment-based lithographic printing ink according to any one of claims 5 to 8, which comprises as printing ink varnishes blends of high boiling distillates and/or vegetable oils, high wetting alkyd resins, highly structured alkyd resins and vegetable resins, and mixtures thereof; or monomers/oligomers/polymers that can be cured by uv-radiation.

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10. A process for the preparation of pigment-based lithographic printing inks according to any one of claims 5 to 9, which comprises incorporating the pigment/solvent dye composition into a printing ink varnish, or one of its components, by shear rate- or heat-inducing methods, and optionally combining the pigment/solvent dye loaded components with the other components of the varnish.

11. A process for the preparation of pigment-based lithographic printing inks according to any one of claims 5 to 9, which comprises incorporating the pigment and the solvent dye separately into a printing ink varnish, or one of its components, by shear- or heat-inducing methods, and optionally combining the pigment and solvent dye loaded components with the other components of the varnish.

12. A process for the preparation of pigment-based lithographic printing inks according to any one of claims 5 to 9, which comprises incorporating the solvent dye as solid or solution in an organic solvent to the finished printing ink, optionally followed by heating.

13. A process for the preparation of pigment-based lithographic printing inks according to any one of claims 5 to 9, which comprises the flushing of presscakes of pigment or pigment/dye mixtures into a varnish medium or a pre-dyed varnish medium.

14. A lithographic printing process which comprises printing a flat substrate with the pigment-based lithographic printing inks according to any one of claims 5 to 9 or with the pigment-based lithographic printing inks prepared according to the processes of claims 10 to 13.

15. A lithographic printing ink colourant, which comprises a mixture of an organic pigment and an organic dyestuff soluble in an organic solvent (solvent dye) wherein the organic pigment is coated with printing ink varnishes (ink vehicles), solvents and other customary additives, the printing ink varnishes or additives being mixed or coloured with the solvent dye either prior to or during pigment processing.

16. The colourant according to claim 15, which comprises 60 to 95% of the organic pigment/solvent dye mixture and 40 to 5% of the printing ink varnishes (ink vehicles), solvent and other customary additives.



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17. The colourant according to claim 15, wherein the pigment/solvent dye ratio is (99-1) : (1-99), preferably (98-10) : (2-90), and most preferred (95-30) : (5-70).

5 18. The colourant according to claim 15, wherein the pigment/solvent dye ratio is (95-65) : (5-35).

19. A pigment-based lithographic printing ink, which comprises the colourants according to any one of claims 15 to 18.

10 20. A process for the preparation of the lithographic printing ink colourants according to any one of claims 15 to 18 which comprises

(a) incorporating the printing ink varnish, which is premixed or coloured with the solvent dye, into an aqueous slurry of the organic pigment, isolating, and optionally drying it, or

15 (b) adding the printing ink varnish to an aqueous slurry of the solvent dye and then combining it with an aqueous slurry of the organic pigment, isolating, and optionally drying it, or

(c) adding the printing ink varnish to an aqueous slurry of a solvent dye/organic pigment combination, isolating, and optionally drying it.

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**AMENDED CLAIMS**

[Received by the International Bureau on 15 March 2005 (15.03.05);  
Original claims 1- 20 replaced by amended claims 1-22]

**+ STATEMENT**

1. A lithographic printing ink composition, characterized in that said composition comprises an organic pigment, an organic dyestuff soluble in an organic solvent (solvent dye), a printing ink varnish (ink vehicle) and a solvent, the printing ink varnish being mixed or coloured with the solvent dye either prior to or during pigment dispersion.
2. The composition as claimed in claim 1, characterized in that said organic dyestuff is a solvent dye selected from the group consisting of C.I. Solvent Red 1, 19, 23, 24, 25, 26, 27, 29, 49, 52, 111, C.I. Solvent Blue 14, 35, 36, 59, 78, C.I. Solvent Yellow 7, 14, 33, 72, 94, 114, C.I. Solvent Orange 1, 2, 7, and mixtures thereof, preferably selected from the group consisting of C.I. Solvent Red 19, 23, 24, 25, 26, 27, 29 and mixtures thereof.
3. The composition as claimed in claim 1 or 2, characterized in that said organic pigment is a disazo or a naphthol pigment.
4. The composition according to any one of claims 1 to 3, wherein the pigment/solvent dye ratio is (99-1) : (1-99), preferably (98-10) : (2-90), and most preferred (95-30) : (5-70).
5. The composition according to any one of claims 1 to 3, wherein the pigment/solvent dye ratio is (95-65) : (5-35).
6. The composition according to any one of claims 1 to 5, which comprises a mixture of solvent dyes and/or a mixture of organic pigments.
7. A pigmented lithographic printing ink, which comprises the composition according to any one of claims 1 to 6.
8. The pigmented lithographic printing ink according to claim 7, which comprises an organic pigment and a solvent dye in a total amount of 0.1-70%, preferably 2 to 55%, by weight, and the remainder being printing ink varnishes, solvents and other customary additives.
9. The pigmented lithographic printing ink according to claims 7 or 8, which is a ready-to-use lithographic printing ink and which comprises the organic pigment and the solvent dye in a total amount of 2 to 20%, preferably 12 to 18%, by weight.

10. A pigmented lithographic printing ink according to claims 7 or 8, which is an ink concentrate and which comprises the organic pigment and the solvent dye in a total amount of 20 to 70%, preferably 20 to 55%, by weight.

11. The pigmented lithographic printing ink according to any one of claims 7 to 10, which comprises as printing ink varnishes blends of high boiling distillates and/or vegetable oils, high wetting alkyd resins, highly structured alkyd resins and vegetable resins, and mixtures thereof; or monomers/oligomers/polymers that can be cured by UV-radiation.

12. A process for the preparation of pigmented lithographic printing inks according to any one of claims 7 to 11, which comprises incorporating the pigment/solvent dye composition into a printing ink varnish, or one of its components, by shear rate- or heat-inducing methods, and optionally combining the pigment/solvent dye loaded components with the other components of the varnish.

13. A process for the preparation of pigmented lithographic printing inks according to any one of claims 7 to 11, which comprises incorporating the pigment and the solvent dye separately into a printing ink varnish, or one of its components, by shear- or heat-inducing methods, and optionally combining the pigment and solvent dye loaded components with the other components of the varnish.

14. A process for the preparation of pigmented lithographic printing inks according to any one of claims 7 to 11, which comprises incorporating the solvent dye as solid or solution in an organic solvent to the finished printing ink, optionally followed by heating.

15. A process for the preparation of pigmented lithographic printing inks according to any one of claims 7 to 11, which comprises the flushing of presscakes of pigment or pigment/dye mixtures into a varnish medium or a pre-dyed varnish medium.

16. A lithographic printing process which comprises printing a flat substrate with the pigmented lithographic printing inks according to any one of claims 7 to 11 or with the pigmented lithographic printing inks prepared according to the processes of claims 12 to 15.

17. A lithographic printing ink colourant, which comprises a solvent, an organic pigment and an organic dyestuff soluble in an organic solvent (solvent dye), wherein the organic pigment is coated with a printing ink varnish (ink vehicle) and the printing ink varnish being mixed or coloured with the solvent dye either prior to or during pigment processing.

18. The colourant according to claim 17, which comprises the organic pigment and the solvent dye in a total amount of 60 to 95%, by weight, and 40 to 5%, by weight, of printing ink varnishes (ink vehicles), solvent and other customary additives.
19. The colourant according to claim 17, wherein the pigment/solvent dye ratio is (99-1) : (1-99), preferably (98-10) : (2-90), and most preferred (95-30) : (5-70).
20. The colourant according to claim 17, wherein the pigment/solvent dye ratio is (95-65) : (5-35).
21. A pigmented lithographic printing ink, which comprises the colourants according to any one of claims 17 to 20.
22. A process for the preparation of the lithographic printing ink colourants according to any one of claims 17 to 20 which comprises
- (a) incorporating the printing ink varnish, which is premixed or coloured with the solvent dye, into an aqueous slurry of the organic pigment, isolating, and optionally drying it, or
  - (b) adding the printing ink varnish to an aqueous slurry of the solvent dye and then combining it with an aqueous slurry of the organic pigment, isolating, and optionally drying it, or
  - (c) adding the printing ink varnish to an aqueous slurry of a solvent dye/organic pigment combination, isolating, and optionally drying it.

Statement under Article 19(1):

The original claims 1 and 15 have been amended by deleting the phrase "other customary additives" in order to more clearly define the scope of the claims. The amendment is based on the text in lines 22 to 23 on page 8 of the original patent specification.

New claim 2 has been added based on the paragraph starting from line 33 on page 3 and ending at line 3 on page 4 as well as Table 1 of the original patent specification.

New claim 3 has been added based on the second paragraph on page 3 of the original patent specification.

In original claims 5 to 14 and in original claim 19, the term "pigment-based" has been replaced by "pigmented" in order to increase the clarity of the claim.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/052741

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B67/08 C09B67/22 C09D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	GB 1 343 606 A (ICI LTD) 16 January 1974 (1974-01-16)  page 2, column 2, line 130 - page 3, column 1, line 20 page 3, column 1, line 49 - line 63 page 3, column 2, line 72 - line 92 examples 15-47 * see esp. example 41 *	1-3, 5-11, 15-20
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

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